

THE EFFECT ON THE LIFETIME OF AN ATOM
UNDERGOING A DIPOLE TRANSITION DUE TO THE
PRESENCE OF A RESONATING ATOM.*

by

Edwin A. Power

University College, Department of Mathematics
London, England

and

University of Wisconsin, Theoretical Chemistry Institute
Madison, Wisconsin

ABSTRACT

The modification of the transition rate from the Einstein A coefficient for an atomic dipole transition due to the presence of a similar atom is obtained without the use of damping theory.

AUTHOR

- - - - -
* This research was supported by National Aeronautics and Space Administration Grant NsG-275-62.

The purpose of this note is to show how the effect of the presence of a similar atom in its ground state on the lifetime of an atom in its first excited state is easily obtained by first order perturbation theory. This is in exact analogy with the calculation of the Einstein A - coefficient and does not need damping theory. Dicke⁽¹⁾ pointed out the changes in lifetime to be expected on symmetry arguments when the two atoms are separated by a distance $R < \lambda$ (λ is the reduced dipole wave length) but still greater than the atomic size. Then the two atoms see essentially the same amplitude of the electric field and dipole selection rules apply to the decay of the combined system. The antisymmetric state is stable the symmetric state has a lifetime one half of the isolated atom. Stephen⁽²⁾ and Hutchinson and Hamaka⁽³⁾ have computed the apparent lifetime as a function of R by using variants of Heitler's damping theory⁽⁴⁾. Here we calculate the lifetime by first order perturbation theory in a manner completely analogous to obtaining the Einstein A coefficient for a radiating isolated atom.

The interaction Hamiltonian for dipole transitions is

$$-\underline{\mu}^{(1)} \cdot \underline{E}^{\perp(1)} - \underline{\mu}^{(2)} \cdot \underline{E}^{\perp(2)} \quad (1)$$

where $\underline{\mu}^{(1)}$ and $\underline{\mu}^{(2)}$ are the dipole moment operator of the two systems. $\underline{E}^{\perp}(\underline{x})$ is the transverse electric field vector which is expanded into the Fourier Series in the volume V

$$\underline{E}^{\perp}(\underline{x}) = \sum_{\substack{\underline{k} \\ \lambda=1,2}} \sqrt{\frac{2\pi\hbar\omega}{V}} i \underline{e}^{(\lambda)}(\underline{k}) \left[a^{(\lambda)}(\underline{k}) e^{i\underline{k}\cdot\underline{x}} - a^{(\lambda)\dagger}(\underline{k}) e^{-i\underline{k}\cdot\underline{x}} \right] \quad (2)$$

$\omega = kc$ is the circular frequency, \underline{k} the wave vector.

$\underline{e}^{(\lambda)}(\underline{k})$ is a unit vector along the direction of polarization for the wave-vector \underline{k} and polarization $\lambda = 1$ or 2 . Due to the transverse nature of the photon

$$\underline{e}^{(\lambda)}(\underline{k}) \cdot \underline{k} = 0 \quad (3)$$

which gives the two possible values of λ . Finally $a^{(\lambda)}(\underline{k})$ and $a^{(\lambda)\dagger}(\underline{k})$ are the annihilation and creation operators for photons of mode \underline{k}, λ and satisfy the commutation relations

$$\left[a^{(\lambda)}(\underline{k}), a^{(\lambda')\dagger}(\underline{k}') \right] = \delta_{\lambda, \lambda'} \delta_{\underline{k}, \underline{k}'} \quad (4)$$

Since the interaction (1) is linear in the electric field first order perturbation theory is sufficient to give the lowest order non-vanishing matrix element for the transition from $|i\rangle$ to $|f\rangle$. Now from the golden rule

$$\begin{aligned} \omega_{if} &= 2\pi |M_{if}|^2 \rho_f \\ &= 2\pi \sum_{\lambda} \oint d\Omega \left| \langle f | \underline{\mu}^{(1)} \cdot \underline{e}^{(\lambda)} e^{i\underline{k}\cdot\underline{r}_1} + \underline{\mu}^{(2)} \cdot \underline{e}^{(\lambda)} e^{i\underline{k}\cdot\underline{r}_2} | i \rangle \right|^2 \\ &\quad \times \frac{2\pi k^3}{(2\pi)^3} \end{aligned} \quad (5)$$

From the dipole approximation inherent in the interaction (1) neither the variation of $e^{i \underline{k} \cdot \underline{r}_1}$ over molecule (1) nor that of $e^{i \underline{k} \cdot \underline{r}_2}$ over molecule (2).

Thus

$$\omega_{if} = \frac{k^3}{2\pi} \sum_{\lambda} \oint d\Omega \left| \langle f | \underline{\mu}^{(1)} \cdot \underline{e}(\lambda) + \underline{\mu}^{(2)} \cdot \underline{e}(\lambda) e^{i \underline{k} \cdot \underline{R}} | i \rangle \right|^2 \quad (6)$$

The atomic final state is just the two atoms in their ground state

$$|f\rangle = \phi_0(1) \phi_0(2) \quad (7)$$

while the initial state is either of the states

$$|\psi_+\rangle = \frac{1}{\sqrt{2}} [\phi_p(1) \phi_0(2) + \phi_p(2) \phi_0(1)] \quad (8)$$

$$|\psi_-\rangle = \frac{1}{\sqrt{2}} [\phi_p(1) \phi_0(2) - \phi_p(2) \phi_0(1)] \quad (9)$$

So

$$\begin{aligned} \omega_{if}^{\pm} = \frac{k^3}{2\pi} \sum_{\lambda} \oint d\Omega e_i^{(\lambda)} e_j^{(\lambda)} \frac{1}{2} [\mu_i(1) \pm e^{i \underline{k} \cdot \underline{R}} \mu_i(2)] \\ \times [\mu_j(1) \pm e^{-i \underline{k} \cdot \underline{R}} \mu_j(2)] \end{aligned} \quad (10)$$

Now from the transverse nature of the photon, equation 3,

$$\sum_{\lambda} e_i^{(\lambda)} e_j^{(\lambda)} = \delta_{ij} - \hat{k}_i \hat{k}_j \quad - (11)$$

$$\omega_{if}^{\pm} = \frac{k^3}{4\pi} \oint d\Omega (\delta_{ij} - \hat{k}_i \hat{k}_j) \left\{ \mu_{i(1)} \mu_{j(1)} + \mu_{i(2)} \mu_{j(2)} + \right. \\ \left. \pm 2 e^{i \underline{k} \cdot \underline{R}} \mu_{i(2)} \mu_{j(1)} \right\} \quad - (12)$$

The angular integral is elementary

$$\tau_{ij}(kR) \equiv \frac{1}{4\pi} \oint d\Omega (\delta_{ij} - \hat{k}_i \hat{k}_j) e^{i \underline{k} \cdot \underline{R}} \\ = \alpha_{ij} \frac{\sin kR}{kR} + \beta_{ij} \left(\frac{\cos kR}{k^2 R^2} - \frac{\sin kR}{k^3 R^3} \right) \quad - (13)$$

where $\alpha_{ij} = \delta_{ij} - \hat{R}_i \hat{R}_j$ - (14)

and $\beta_{ij} = \delta_{ij} - 3 \hat{R}_i \hat{R}_j$ - (15)

Finally using the necessary hypothesis that the two atoms are identical

$$\omega_{if}^{\pm} = 2 k^3 \mu_i \mu_j [\tau_{ij}(0) \pm \tau_{ij}(kR)] \quad - \quad (16)$$

When $R \ll \lambda$ we are left with the Dicke result; using $\tau_{ij}(0) = \frac{2}{3} \delta_{ij}$ from equation (13)

$$\omega_{if}^{+} = \frac{8}{3} k^3 |\mu|^2 = 2 \omega_{if}(\text{Einstein}) \quad - \quad (17)$$

$$\omega_{if}^{-} = 0 + O(k^5 R^2) |\mu|^2 \quad - \quad (18)$$

On the other hand for large R , $\tau_{ij}(kR) \sim \alpha_{ij} \frac{\sin kR}{kR}$ — (19)

and so $\omega_{if}^{+} = \omega_{if}^{-} = \frac{4}{3} k^3 |\mu|^2$ for $R \gg \lambda$
 $= \omega_{if}(\text{Einstein}) \quad - \quad (20)$

ACKNOWLEDGEMENTS

It is a pleasure to thank Dr. William J. Meath for helpful discussions.

REFERENCES

1. R.H. Dicke, Phys. Rev. 93, 99 (1954)
2. M.J. Stephen, J. Chem. Phys., 40, 669 (1964)
3. D.A. Hutchinson and H.F. Hameka, J. Chem. Phys., 41, 2006 (1964)
4. W. Heitler, The Quantum Theory of Radiation, (Oxford University Press, London 1954) pp. 163-174.